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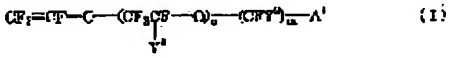
(54) FLUORINE-CONTAINING MOLDING, ITS PRODUCING METHOD, FLUORINE-CONTAINING POLYMER, AND ITS PRODUCING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a fluorine-containing molding excellent in shape stability, and to provide a producing method of the fluorine-containing polymer.
SOLUTION: The fluorine-containing polymer is obtained by polymerizing a perfluoro- vinyl ether derivative represented by formula (1) wherein Y1 is a halogen atom or a perfluoro-alkyl group; Y2 is a halogen atom; A1 is -SO2X1 [wherein X1 is a halogen atom, -OM1 [wherein M1 is a hydrogen atom, an alkali metal or NR3R4R5R6 (wherein R3, R4, R5 and R6 are each a hydrogen atom, or a 1-4C alkyl group)], -OM21/2 [M2 is an alkaline earth metal], or -NR1R2 [wherein R1 and R2 are each a hydrogen atom, an alkali metal, an alkyl group, or a sulfonyl-containing group]], or -COZ1 [Z1 is a hydroxy group, -NR7R8 [R7 and R8 are each a hydrogen atom, an alkali metal, an alkyl group, and a sulfonyl-containing group], or a 1-4C alkoxy group].



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CLAIMS

[Claim(s)]
[Claim 1]
The following general formula (I)
[Formula 1]

$$CF_2=CF-O-(CF_2\underset{Y^1}{CF}-O)_n-(CFY^2)_m-A^1 \qquad (I)$$

(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A1 expresses -SO 2X1 or -COZ1. X1 expresses a halogen atom, -OM1, -OM 21/2, or -NR one R2. M1 expresses a hydrogen atom, alkali metal, or NR three R4R5R6, and R3, R4, R5, and R6 are the same -- or it differs and a hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed. M2 expresses alkaline earth metal. R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z1 expresses the alkoxyl group of hydroxyl, -NR seven R8, or carbon numbers 1-4. R7 and R8 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. the fluorine-containing polymer obtained by carrying out the polymerization of the perfluoro vinyl ether derivative expressed -- it is
eta (0.1)/eta (10) is two or more.
The fluorine-containing polymer characterized by things.
[Claim 2]
The fluorine-containing polymer according to claim 1 which is the 2 yuan or more copolymer obtained by carrying out the polymerization of a perfluoro vinyl ether derivative and the ethylene nature monomer.
[Claim 3]
An ethylene nature monomer is a fluorine-containing polymer according to claim 2 which is tetrafluoroethylene.
[Claim 4]
It is the fluorine-containing polymer according to claim 1, 2, or 3 whose Y2 Y1 is a trifluoromethyl radical and is a fluorine atom, whose n is 0 or 1 and whose m is 2.
[Claim 5]
It is the fluorine-containing polymer manufacture approach which consists of manufacturing a fluorine-containing polymer according to claim 1, 2, 3, or 4,
It has the process at which fluorine gas is contacted.
The fluorine-containing polymer manufacture approach characterized by things.
[Claim 6]

It is the fluorine-containing polymer manufacture approach which consists of manufacturing a fluorine-containing polymer according to claim 1, 2, 3, or 4,
The following general formula (I)
[Formula 2]

$$CF_2=CF-O-(CF_2\underset{Y^1}{CF}-O)_n-(CFY^2)_m-A^1 \qquad (I)$$

(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A1 expresses -SO 2X1 or -COZ1. X1 expresses a halogen atom, -OM1, -OM 21/2, or -NR one R2. M1 expresses a hydrogen atom, alkali metal, or NR three R4R5R6, and R3, R4, R5, and R6 are the same -- or it differs and a hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed. M2 expresses alkaline earth metal. R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z1 expresses the alkoxyl group of hydroxyl, -NR seven R8, or carbon numbers 1-4. R7 and R8 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. The whole quantity of a perfluoro vinyl ether derivative expressed is taught, and it has the process which makes a polymerization reaction start.
The fluorine-containing polymer manufacture approach characterized by things.
[Claim 7]
It is the fluorine-containing polymer manufacture approach which consists of manufacturing a fluorine-containing polymer according to claim 1, 2, 3, or 4,
It has the process which blends a fluorine polymer (P) and a fluorine polymer (Q),
Said fluorine polymer (P) and said fluorine polymer (Q),
The following general formula (I)
[Formula 3]

$$CF_2=CF-O-(CF_2\underset{Y^1}{CF}-O)_n-(CFY^2)_m-A^1 \qquad (I)$$

(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A1 expresses -SO 2X1 or -COZ1. X1 expresses a halogen atom, -OM1, -OM 21/2, or -NR one R2. M1 expresses a hydrogen atom, alkali metal, or NR three R4R5R6, and R3, R4, R5, and R6 are the same -- or it differs and a hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed. M2 expresses alkaline earth metal. R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z1 expresses the alkoxyl group of hydroxyl, -NR seven R8, or carbon numbers 1-4. R7 and R8 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative expressed -- it is
the mol of the perfluoro vinyl ether derivative unit in said fluorine polymer (P) -- a ratio [(p-q) /q] (however, it is p>q.) with conversion content [p %] and mol conversion content [q% of the perfluoro vinyl ether derivative unit in said fluorine polymer (Q)] is 0.5 or more

The fluorine-containing polymer manufacture approach characterized by things.
[Claim 8]
It is the fluorine-containing polymer manufacture approach which consists of manufacturing a fluorine-containing polymer according to claim 1, 2, 3, or 4,
It has the process which blends a fluorine polymer (R) and a fluorine polymer (S),
Said fluorine polymer (R) and said fluorine polymer (S) are the following general formula (I).
[Formula 4]

$$CF_2=CF-O-(CF_2\underset{Y^1}{CF}-O)_n-(CFY^2)_m-A^1 \qquad (I)$$

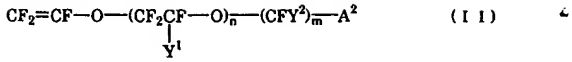
(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A1 expresses -SO 2X1 or -COZ1. X1 expresses a halogen atom, -OM1, -OM 21/2, or -NR one R2. M1 expresses a hydrogen atom, alkali metal, or NR three R4R5R6, and R3, R4, R5, and R6 are the same -- or it differs and a hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed. M2 expresses alkaline earth metal. R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z1 expresses the alkoxyl group of hydroxyl, -NR seven R8, or carbon numbers 1-4. R7 and R8 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative expressed -- it is
The ratio [r/s] (however, it is r>s.) of the melt flow rate [r (g / 10 minutes)] of said fluorine polymer (R) and the melt flow rate [s (g / 10 minutes)] of said fluorine polymer (S) is ten or more.
The fluorine-containing polymer manufacture approach characterized by things.
[Claim 9]
It is manufactured by the fluorine-containing polymer manufacture approach according to claim 5, 6, 7, or 8.
The fluorine-containing polymer characterized by things.
[Claim 10]
Fluorine gas is contacted and it consists of acquiring the fluorine-containing Plastic solid eta (0.1)/whose eta (10) is two or more, after fabricating a perfluoro vinyl ether derivative using the fluorine-containing polymer used as 1 monomer component at least.
The fluorine-containing Plastic solid manufacture approach characterized by things.
[Claim 11]
It is obtained from performing alkali hydrolysis or acid treatment to a fluorine-containing polymer according to claim 1, 2, 3, 4, or 9,
It has the sulfonic group which may form the metal salt.
The fluorine-containing polymer derivative characterized by things.
[Claim 12]
A fluorine-containing polymer is the following general formula (II).
[Formula 5]

$$CF_2=CF-O-(CF_2\underset{Y^1}{CF}-O)_n-(CFY^2)_m-A^2 \qquad (II)$$

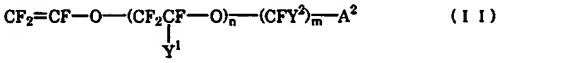
(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A2 expresses -SO 2X2 or -COZ2. X2 expresses a halogen atom or -NR one R2, and R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z2 expresses the alkoxyl group of -NR seven R8 or carbon numbers 1-4. R7 and R8 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. the fluorine-containing polymer (T) obtained by carrying out the polymerization of the perfluoro vinyl ETERUN acid derivative (T1) expressed -- it is
A fluorine-containing polymer derivative is a fluorine-containing polymer derivative according to claim 11 from which said X2 in said fluorine-containing polymer (T) or said Z2 is changed into -OM3 or -OM 41/2 (M3 expresses a hydrogen atom or alkali metal, and M4 expresses alkaline earth metal.).
[Claim 13]
It is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing a fluorine-containing polymer derivative according to claim 11 or 12,
It has the process at which fluorine gas is contacted, and the process which carries out precursor processing.
The fluorine-containing polymer derivative manufacture approach characterized by things.
[Claim 14]
It is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing a fluorine-containing polymer derivative according to claim 11 or 12,
The following general formula (II)
[Formula 6]

$$CF_2=CF-O-(CF_2\underset{Y^1}{CF}-O)_n-(CFY^2)_m-A^2 \qquad (II)$$

(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A2 expresses -SO 2X2 or -COZ2. X2 expresses a halogen atom or -NR one R2, and R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z2 expresses the alkoxyl group of -NR seven R8 or carbon numbers 1-4. R7 and R8 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. The whole quantity of a perfluoro vinyl ether derivative (T1) expressed is taught, and it has the process which makes a polymerization reaction start, and the process which carries out precursor processing.
The fluorine-containing polymer derivative manufacture approach characterized by things.
[Claim 15]
It is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing a fluorine-containing polymer derivative according to claim 11 or 12,
It has the process which blends a fluorine polymer (PT) and a fluorine polymer (QT), and the process which carries out precursor processing.
Said fluorine polymer (PT) and said fluorine polymer (QT) are the following general formula (II).
[Formula 7]



(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) q expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A2 expresses -SO 2X2 or -COZ2. X2 expresses a halogen atom or -NR one R2, and R1 and R2 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z2 expresses the alkoxyl group of -NR seven R8 or carbon numbers 1-4. R7 and R8 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative (T1) expressed — it is
the mol of the perfluoro vinyl ether derivative (T1) unit in said fluorine polymer (PT) -- the fluorine-containing polymer derivative manufacture approach characterized by a ratio [(pt-qt) /qt] (however, it being pt>qt.) with conversion content [pt%] and mol conversion content [qt% of the perfluoro vinyl ether derivative (T1) unit in said fluorine polymer (QT)] being 0.5 or more.
[Claim 16]
It is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing a fluorine-containing polymer derivative according to claim 11 or 12.
It has the process which blends a fluorine polymer (RT) and a fluorine polymer (ST), and the process which carries out precursor processing.
Said fluorine polymer (RT) and said fluorine polymer (ST) are the following general formula (II).
[Formula 8]



(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A2 expresses -SO 2X2 or -COZ2. X2 expresses a halogen atom or -NR one R2, and R1 and R2 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z2 expresses the alkoxyl group of -NR seven R8 or carbon numbers 1-4. R7 and R8 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative (T1) expressed — it is
The ratio [rt/st] (however, it is rt>st.) of the melt flow rate [rt (g / 10 minutes)] of said fluorine polymer (RT) and the melt flow rate [st (g / 10 minutes)] of said fluorine polymer (ST) is ten or more.
The fluorine-containing polymer derivative manufacture approach characterized by things.
[Claim 17]
It is manufactured by the fluorine-containing polymer derivative manufacture approach according to claim 13, 14, 15, or 16.
The fluorine-containing polymer derivative characterized by things.
[Claim 18]
It fabricates using a fluorine-containing polymer derivative according to claim 11, 12, or 17, and

consists of acquiring a fluorine-containing Plastic solid.
The fluorine-containing Plastic solid manufacture approach characterized by things.
[Claim 19]
It fabricates using claims 1, 2, 3, and 4 or a fluorine-containing polymer given in nine and/or claims 11 and 12, or a fluorine-containing polymer derivative given in 17.
The fluorine-containing Plastic solid characterized by things.
[Claim 20]
It is manufactured by the fluorine-containing Plastic solid manufacture approach according to claim 10 or 18.
The fluorine-containing Plastic solid characterized by things.
[Claim 21]
The fluorine-containing Plastic solid according to claim 19 or 20 which is the film.
[Claim 22]
It is the fluorine-containing Plastic solid fabricated using claims 1, 2, 3, and 4 or a fluorine-containing polymer given in nine and/or claims 11 and 12, or a fluorine-containing polymer derivative given in 17.
The thickness of said fluorine-containing Plastic solid is 10-200 micrometers.
The fluorine-containing Plastic solid characterized by things.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to a fluorine-containing Plastic solid, the fluorine-containing Plastic solid manufacture approach, a fluorine-containing polymer, and the fluorine-containing polymer manufacture approach.
[0002]
[Description of the Prior Art]
The Plastic solid of a fluorine-containing sulfonic acid type polymer with which halo sulfonyl group [-SO2X;X has sulfonic acid type functional groups, such as halogen atom], a sulfonic group, or its salt, is used for the cation exchange membrane for alkali electrolysis, the diaphragm for fuel cells, etc. as an electrolyte membrane excellent in chemical stability. A sulfonic group or its salt can be guided from a halo sulfonyl group.
[0003]
A fluorine-containing sulfonic acid type polymer needs to be in the condition that water was included in large quantities, in order to demonstrate the engine performance as an electrolyte membrane or ion exchange membrane. However, in such the condition, an electrolyte membrane and ion exchange membrane changed into the condition of having swollen with water, become weak mechanically, and it is torn, or they tended to cause plastic deformation, and had the problem of being configuration instability.
[0004]
As an approach of solving this problem, the method of performing chemistry bridge formation is proposed by JP,2000-188013,A. However, since melting shaping is carried out, the fluorine-containing sulfonic acid type polymer is usually difficult for acquiring the Plastic solid using the fluorine-containing sulfonic acid type polymer over which the bridge was constructed.
[0005]
As an approach of making a fluorine-containing sulfonic acid type polymer constructing a bridge, the approach of constructing a bridge with heating, the approach of irradiating ultraviolet rays or a radiation using a cross linking agent, etc. are mentioned to others. However, since shaping and bridge formation took place to coincidence by heating a fluorine-containing sulfonic acid type polymer in the case of the approach of constructing a bridge with heating, there was a problem that shaping became difficult.
[0006]
In the case of the approach of irradiating ultraviolet rays or a radiation using a cross linking agent, after mixing the cross linking agent before carrying out melting shaping, and carrying out melting shaping, ultraviolet rays or a radiation was irradiated, but there were a problem that a cross linking agent will deteriorate, and a problem that it would be accompanied by decomposition of a fluorine-containing sulfonic acid type polymer if a radiation is used under the temperature of 250-300 degrees C which is the melting molding temperature of a fluorine-containing sulfonic acid type polymer.
[0007]

In the structure of cross linkage obtained by the approach of constructing a bridge with heating, or the approach of irradiating ultraviolet rays or a radiation using a cross linking agent, when a Plastic solid was used as the cation exchange membrane for alkali electrolysis, a diaphragm for fuel cells, etc., there was a problem of decomposing at the time of a generation of electrical energy of a fuel cell and electrolysis of salt.
[0008]
[Problem(s) to be Solved by the Invention]
The purpose of this invention is to provide the fluorine-containing Plastic solid excellent in configuration stability, such as plastic deformation, and its manufacture approach, and a list with a fluorine-containing polymer and its manufacture approach in view of the above-mentioned present condition.
[0009]
[Means for Solving the Problem]
This invention is the following general formula (I).
[0010]
[Formula 9]

$$CF_2=CF-O-(CF_2\underset{\displaystyle Y^1}{\underset{|}{C}}F-O)_n-(CFY^2)_m-A^1 \qquad (I)$$

[0011]
(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A1 expresses -SO 2X1 or -COZ1. X1 expresses a halogen atom, -OM1, -OM 21/2, or -NR one R2. M1 expresses a hydrogen atom, alkali metal, or NR three R4R5R6, and R3, R4, R5, and R6 are the same — or it differs and a hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed. M2 expresses alkaline earth metal. R1 and R2 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z1 expresses the alkoxyl group of hydroxyl, -NR seven R8, or carbon numbers 1-4. R7 and R8 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. It is the fluorine-containing polymer obtained by carrying out the polymerization of the perfluoro vinyl ether derivative expressed, and the above-mentioned fluorine-containing polymer is a fluorine-containing polymer characterized by eta (0.1)/eta (10) being two or more.
[0012]
This invention is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer again, and is the fluorine-containing polymer manufacture approach characterized by having the process at which fluorine gas is contacted.
This invention is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer again, and is the fluorine-containing polymer manufacture approach characterized by having the process which the whole quantity of a perfluoro vinyl ether derivative expressed with the above-mentioned general formula (I) is taught [process], and makes a polymerization reaction start.
[0013]
This invention is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer again. It has the process which blends a fluorine polymer (P) and a fluorine polymer (Q). The above-mentioned fluorine polymer (P) and the above-mentioned fluorine polymer (Q) mol conversion content [p% of a perfluoro vinyl ether derivative unit [in / the polymerization of the perfluoro vinyl ether derivative

expressed with the above-mentioned general formula (I) is carried out, and it is obtained, and / the above-mentioned fluorine polymer (P)] —] — A ratio with mol conversion content [q%] of the perfluoro vinyl ether derivative unit in the above-mentioned fluorine polymer (Q) [(p-q) /q] (however, it is p>q.) It is the fluorine-containing polymer manufacture approach characterized by being 0.5 or more.
[0014]
This invention is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer again. It has the process which blends a fluorine polymer (R) and a fluorine polymer (S). The above-mentioned fluorine polymer (R) and the above-mentioned fluorine polymer (S) It is what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative expressed with the above-mentioned general formula (I). The melt flow rate of the above-mentioned fluorine polymer (R) [r (g / 10 minutes)], A ratio with the melt flow rate [s (g / 10 minutes)] of the above-mentioned fluorine polymer (S) [r/s] (however, it is r>s.) It is the fluorine-containing polymer manufacture approach characterized by being ten or more.
[0015]
This invention is the fluorine-containing Plastic solid manufacture approach characterized by consisting of contacting fluorine gas and acquiring the fluorine-containing Plastic solid eta (0.1)/whose eta (10) is two or more, after fabricating a perfluoro vinyl ether derivative again using the fluorine-containing polymer used as 1 monomer component at least. Hereafter, it is called the fluorine-containing Plastic solid manufacture approach (1) of this invention.
[0016]
This invention is a fluorine-containing polymer derivative characterized by having the sulfonic group which is obtained again from performing alkali hydrolysis or acid treatment to the above-mentioned fluorine-containing polymer, and may form the metal salt.
This invention is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative again, and is the fluorine-containing polymer derivative manufacture approach characterized by having the process at which fluorine gas is contacted, and the process which carries out precursor processing. Hereafter, it is called the fluorine-containing polymer derivative manufacture approach (A) of this invention.
[0017]
This invention is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative again, and is the following general formula (II).
[0018]
[Formula 10]

$$CF_2=CF-O-(CF_2\underset{\displaystyle Y^1}{\underset{|}{C}}F-O)_n-(CFY^2)_m-A^2 \qquad (II)$$

[0019]
(Y1 expresses a halogen atom or a perfluoroalkyl radical among a formula.) n expresses the integer of 0-3, and n Y1 may be the same and may differ. Y2 expresses a halogen atom. m expresses the integer of 1-5, and m Y2 may be the same and may differ. A2 expresses -SO 2X2 or -COZ2. X2 expresses a halogen atom or -NR one R2, and R1 and R2 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. Z2 expresses the alkoxyl group of -NR seven R8 or carbon numbers 1-4. R7 and R8 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. It is the fluorine-containing polymer derivative manufacture

approach characterized by having the process which the whole quantity of a perfluoro vinyl ether derivative (T1) expressed is taught [process], and makes a polymerization reaction start, and the process which carries out precursor processing. Hereafter, it is called the fluorine-containing polymer derivative manufacture approach (B) of this invention.
[0020]
This invention is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative again. It has the process which blends a fluorine polymer (PT) and a fluorine polymer (QT), and the process which carries out precursor processing. The above-mentioned fluorine polymer (PT) and the above-mentioned fluorine polymer (QT) It is what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative (T1) expressed with the above-mentioned general formula (II). Mol conversion content [pt%] of the perfluoro vinyl ether derivative (T1) unit in the above-mentioned fluorine polymer (PT), A ratio with mol conversion content [qt%] of the perfluoro vinyl ether derivative (T1) unit in the above-mentioned fluorine polymer (QT) [(pt-qt) /qt] (however, it is pt>qt.) It is the fluorine-containing polymer derivative manufacture approach characterized by being 0.5 or more. Hereafter, it is called the fluorine-containing polymer derivative manufacture approach (C) of this invention.
[0021]
This invention is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative again. It has the process which blends a fluorine polymer (RT) and a fluorine polymer (ST), and the process which carries out precursor processing. The above-mentioned fluorine polymer (RT) and the above-mentioned fluorine polymer (ST) It is what is obtained by carrying out the polymerization of the perfluoro vinyl ether derivative (T1) expressed with the above-mentioned general formula (II). The melt flow rate of the above-mentioned fluorine polymer (RT) [rt (g / 10 minutes)], A ratio with the melt flow rate [st (g / 10 minutes)] of the above-mentioned fluorine polymer (ST) [rt/st] (however, it is rt>st.) It is the fluorine-containing polymer derivative manufacture approach characterized by being ten or more. Hereafter, it is called the fluorine-containing polymer derivative manufacture approach (D) of this invention.
[0022]
It is the fluorine-containing Plastic solid manufacture approach characterized by this invention consisting of fabricating using the above-mentioned fluorine-containing polymer derivative, and acquiring a fluorine-containing Plastic solid again. Hereafter, it is called the fluorine-containing Plastic solid manufacture approach (2) of this invention.
This invention is a fluorine-containing Plastic solid characterized by fabricating using the above-mentioned fluorine-containing polymer and/or the above-mentioned fluorine-containing polymer derivative again.
[0023]
This inventions are the above-mentioned fluorine-containing polymer and/or a fluorine-containing Plastic solid fabricated using the above-mentioned fluorine-containing polymer derivative again, and the above-mentioned fluorine-containing Plastic solid is a fluorine-containing Plastic solid characterized by thickness being 10-200 micrometers.
This invention is explained below at a detail.
[0024]
After the fluorine-containing Plastic solid manufacture approach (1) of this invention fabricates a perfluoro vinyl ether derivative using the fluorine-containing polymer used as 1 monomer component at least, it contacts fluorine gas and consists of acquiring the fluorine-containing Plastic solid eta (0.1)/whose eta (10) is two or more. Although the above "a monomer component" may be a monomer which serves as a fluorine-containing polymer by carrying out a polymerization, the number of the above-mentioned monomers may be one and you may be two or more sorts. the above-mentioned perfluoro vinyl ether derivative is used for the above-mentioned fluorine-containing polymer as at least one sort of the above-mentioned monomer.
In this specification, it may be called "fluoridization" to contact fluorine gas.
[0025]

The above-mentioned fluoridization is performed by contacting fluorine gas on the processing prefabrication object in front of the fluoridization which fabricates a fluorine-containing polymer and is obtained. the fluorine gas to be used -- fluorine gas -- although it may be independent, since the reaction of fluorine gas and the above-mentioned processing prefabrication object is intense exothermic reaction, it is desirable to dilute and use fluorine gas with inert gas, such as nitrogen gas and argon gas, from the point which controls the point and reaction which avoid risk. As the above-mentioned inert gas, nitrogen gas is desirable. As for the rate of fluorine gas and inert gas, it is desirable that it is 5:95-25:75 in the volume ratio under isothermal isotonic.

[0026]

As for the above-mentioned fluoridization, it is desirable to carry out at the temperature of 25-200 degrees C. A more desirable minimum is 70 degrees C and a more desirable upper limit is 150 degrees C. Although the above-mentioned fluoridization is based also on the temperature which performs the fluoridization, it is desirable to carry out for 10 minutes to 12 hours. Although the above-mentioned fluoridization may be performed under pressurization, it is desirable to carry out dilution fluorine gas to the processing prefabrication object placed into the reactor with through continuously or intermittently under atmospheric pressure or fine pressurization.

[0027]

The above-mentioned fluoridization can construct a bridge in a processing prefabrication object by contacting fluorine gas. By the above-mentioned fluoridization, the fluorine-containing polymer molecule in a front [processing] Plastic solid produces new association among other fluorine-containing polymer molecules, or a fluorine-containing polymer molecule produces new association in intramolecular, macromolecule quantification is carried out and it is thought that three-dimensions network structure is formed. removing the impurity which a processing prefabrication object has, while the above-mentioned fluoridization makes a processing prefabrication object construct a bridge **** -- processing prefabrication -- the unstable end group which a fluorine-containing polymer in the living body has can be stabilized. In this specification, the above "an unstable end group" means the radical which changes chemically easily with heating etc., for example, -COF, -COOH, -COOCH3, -CONH2, -CH2OH, etc. are mentioned. If the Plastic solid which has the above-mentioned unstable end group is used as an electrolyte membrane or an ion exchange membrane, a carboxyl group etc. may carry out a decarboxylation and a Plastic solid may foam. Moreover, a Plastic solid may color with the carbon which a carboxyl group etc. disassembles and produces. By giving the above-mentioned fluoridization, it is thought that the above-mentioned unstable end group can be made into a stable trifluoromethyl radical, and it can control that a fluorine-containing Plastic solid foams and colors.

[0028]

After fabricating the fluorine-containing Plastic solid manufacture approach (1) of this invention using a fluorine-containing polymer, it performs the above-mentioned fluoridization. If a fluorine-containing polymer carries out macromolecule quantification, since melt viscosity will become high too much and a moldability will get worse by the above-mentioned fluoridization, before performing the fluoridization, fabricating in a desired configuration is desirable.

[0029]

The fluorine-containing polymer used for the fluorine-containing Plastic solid manufacture approach (1) of this invention carries out the polymerization of the perfluoro vinyl ether derivative (henceforth "a compound (I)") expressed with an above-mentioned general formula (I), and is obtained.

[0030]

n [in / in the above-mentioned compound (I) / the above-mentioned general formula (I)] expresses the integer of 0-3. Above n is 0 or 1 and is 0 more preferably. m in the above-mentioned general formula (I) expresses the integer of 1-5. It is 1 and is 2 more preferably.

[0031]

Y1 in the above-mentioned general formula (I) expresses a halogen atom or a perfluoroalkyl radical, and n Y1 may be the same and may differ. Y2 in the above-mentioned general formula (I) expresses a halogen atom, and m Y2 may be the same and may differ. Although it may not be

limited especially as a halogen atom of the above Y1 and Y2 but you may be any of a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom, it is a fluorine atom preferably. It is not limited especially as the above-mentioned perfluoroalkyl radical, for example, a trifluoromethyl radical, a pentafluoro ethyl group, etc. are mentioned. In the above-mentioned general formula (I), it is desirable that Y1 is a perfluoroalkyl radical, it is more desirable that it is a trifluoromethyl radical, and, as for Y2, it is desirable that it is a fluorine atom.

[0032]

A1 in the above-mentioned general formula (I) expresses -SO 2X1 or -CO2I. The above X1 expresses a halogen atom, -OM1, -OM 21/2, or -NR one R2. the above M1 expresses a hydrogen atom, alkali metal, or NR three R4R5R6, and R3, R4, R5, and R6 are the same -- or it differs and a hydrogen atom or the alkyl group of carbon numbers 1-4 is expressed. The above M2 expresses alkaline earth metal. R1 and R2 are the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed.

[0033]

Although the same thing as the above Y1 and Y2 is mentioned as a halogen atom of the above X1, the halogen atom of the above X1, the halogen atom of Y1, and the halogen atom of Y2 may be the same, and may differ from each other. It is not limited especially as an alkali metal of the above M1, for example, Li, Na, K, Cs, etc. are mentioned. It may not be limited especially as an alkyl group of the above R3, R4, R5, and R6, for example, you may be the alkyl group of the shape of a straight chain of carbon numbers 1-4, and the letter of branching, and a methyl group, an ethyl group, a propyl group, an isopropyl group, etc. are mentioned as such an alkyl group, for example. It is not limited especially as an alkaline earth metal of the above M2, for example, Mg, calcium, etc. are mentioned.

[0034]

It is not limited especially as an alkali metal of the above R1 and R2, for example, the same thing as the alkali metal of the above M1 etc. is mentioned. It is not limited especially as an alkyl group of the above R1 and R2, for example, the alkyl group of the carbon numbers 1-4, such as a methyl group and an ethyl group, etc. is mentioned. The alkyl group of the above R1 and R2 may be permuted by the halogen atom. The fluorine-containing alkyl sulfonyl group which is a fluorine-containing alkyl group in which the above-mentioned sulfonyl content radical has a sulfonyl group, for example, may have the substituent at the end is mentioned, and -SO2Rf 1Z3 (Rf1 expresses a fluorine-containing alkylene group, and Z3 expresses an organic radical.) etc. is mentioned as the above-mentioned fluorine-containing alkyl sulfonyl group, for example. As the above-mentioned organic radical, -SO2F were mentioned, and -SO 2X1 in A1 of the above-mentioned general formula (I) may be connected with infinity like -SO2(NR1SO2Rf1SO2) kNR1SO2- (k shows one or more integers.), for example, when the above X1 is -NR one R2.

[0035]

The above Z1 expresses the alkoxyl group of hydroxyl, -NR seven R8, or carbon numbers 1-4. the above R7 and R8 is the same -- or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. As the above R7 and R8, the same thing as the above R1 and R2 etc. is mentioned, and the above R1, R2, R7, and R8 may be the same, and may differ. It may not be limited especially as the above-mentioned alkoxyl group, for example, you may be the alkoxyl group of the shape of a straight chain of carbon numbers 1-4, and the letter of branching, and -OCH3, -OC2H5, -OC3H7, -OCH (CH3)2, etc. are mentioned as such an alkoxyl group, for example. The above-mentioned alkoxyl group may be permuted by the halogen atom.

[0036]

In this invention, m is 2, as the above-mentioned compound (I), n in the above-mentioned general formula (I) is 0, and that whose X1 is a fluorine atom is [Y2 is a fluorine atom and / A1 is -SO 2X1, and] desirable [1].

[0037]

As for the above-mentioned fluorine-containing polymer, it is usually desirable that it is the copolymer of the above-mentioned compound (I), and the above-mentioned compound (I) and a copolymerizable monomer, and is the 2 yuan or more copolymer obtained by carrying out the

polymerization of the above-mentioned compound (I) and the ethylene nature monomer. At least one sort of above-mentioned 2 yuan or more copolymers are obtained using at least one sort and the above-mentioned ethylene nature monomer in the above-mentioned compound (I). The above-mentioned ethylene nature monomer will not be limited especially if it has a vinyl group, but it differs from the above-mentioned compound (I).

[0038]

As the above-mentioned ethylene nature monomer, the fluorine content ethylene nature monomer which has a fluorine atom, and the fluorine non-containing ethylene nature monomer which does not have a fluorine atom are mentioned, and it is not limited especially as the above-mentioned fluorine content ethylene nature monomer, for example, is following general formula

CF2=CF-Rf2.

(-- among a formula, Rf2 expresses -F, -Cl, -Rf3, or -ORf3, and Rf3 expresses the fluoro alkyl group of the shape of a straight chain which may have ether oxygen of carbon numbers 1-9, and the letter of branching.) -- the halo ethylene nature monomer expressed and the following general formula

CHY3=CFY4

the inside of a formula, and Y3 -H or -F -- expressing -- Y4 -H, -F, and - Cl, Rf4, or -ORf4 is expressed. Rf4 expresses the fluoro alkyl group of the shape of a straight chain which may have ether oxygen of carbon numbers 1-9, and the letter of branching. The hydrogen content fluoro ethylene nature monomer expressed is mentioned.

[0039]

It is not limited especially as the above-mentioned fluorine non-containing ethylene nature monomer, for example, ethylene, a propylene, 1-butene, 2-butene, etc. are mentioned.

As for the above-mentioned ethylene nature monomer, it is desirable that it is at least one chosen from the group which consists of fluoro vinyl ether expressed with CF2=CF2, CH2=CF2, CF2=CFCl, CF2=CFH, CH2=CFH, CF2=CFCF3, and CF2=CF-O-Rf5 (Rf5 expresses the fluoro alkyl group of carbon numbers 1-9 or the fluoropoly ether group of carbon numbers 1-9 among a formula.). As for the above-mentioned fluoro vinyl ether, it is desirable that the carbon number of Rf5 is the perfluoroalkyl radical of 1-3.

[0040]

As for the above-mentioned ethylene nature monomer, it is desirable that they are a par halo ethylene nature monomer, especially a perfluoro ethylene nature monomer, and it is more desirable that it is CF2=CF2. When one sort or two sorts or more can be used and it uses two or more sorts of above-mentioned ethylene nature monomers as the above-mentioned ethylene nature monomer, a fluorine content ethylene nature monomer and a fluorine non-containing ethylene nature monomer may be used.

[0041]

Besides the above-mentioned ethylene nature monomer, further, in order to give various functions to the above-mentioned fluorine-containing polymer, other copolymerizable monomers may be added in the range which does not spoil the fundamental engine performance as a fluorine-containing polymer. It is not limited especially as the above and other copolymerizable monomers, for example, is suitably chosen from copolymerizable monomers according to the purposes, such as control of mechanical physical properties, such as control of a rate of polymerization, control of a polymer presentation, and an elastic modulus, and installation of a bridge formation site, and the monomer which has a radical originating in the monomer which has two or more unsaturated bonds, such as a divinylbenzene, the monomer containing a cyano group, a carboxyl group, and/or a carboxyl group, the monomer which has a halogen atom at the end are mentioned.

[0042]

Although it is not limited especially as an approach of carrying out the polymerization of the above-mentioned compound (I) but a well-known approach can be used conventionally, for example, solution polymerization, an emulsion polymerization, etc. are mentioned, and an emulsion polymerization is desirable especially. The class of polymerization initiator used by the above-mentioned polymerization, concentration and polymerization temperature, and the

polymerization preassure force can use a well-known thing conventionally.

[0043]

eta (0.1)/eta (10) of the above-mentioned fluorine-containing polymer is two or more. Since the mechanical strength of the Plastic solid which fabricates a fluorine-containing polymer as Above eta (0.1)/eta (10) is less than two, and is acquired is inadequate, it is torn or there is a possibility of becoming configuration instability, such as causing plastic deformation. The desirable minimum of Above eta (0.1)/eta (10) is [7 and the still more desirable minimum of 4 and a more desirable minimum] 10. The mechanical strength of eta [eta (0.1)/] (10) of the above-mentioned fluorine-containing polymer improves so that a value is large, but since melting shaping may become difficult, when carrying out melting shaping later, a desirable upper limit is 20. In this specification, the above "eta (0.1)/eta (10)" expresses the value which **(ed) the value eta of the viscosity measured on the frequency of 0.1 rads/second (0.1) by value [of the viscosity measured on the frequency of ten rads/second] eta (10).

[0044]

In the fluorine-containing Plastic solid manufacture approach (1) of this invention, since macromolecule quantification can be constructed a bridge and carried out by performing the above-mentioned fluoridization as a molding material for fabricating the processing prefabrication object which is the object which performs the fluoridization, eta (0.1)/eta (10) may be less than two fluorine polymer. In this specification, the above "a fluorine polymer" means what is obtained by carrying out the polymerization of the above-mentioned compound (I). eta (0.1)/eta (10) may be less than two, and eta (0.1)/eta (10) of the above-mentioned fluorine polymer may be two or more. The above-mentioned fluorine polymer is the point that eta (0.1)/eta (10) may be less than two, and the above-mentioned fluorine-containing polymers eta (0.1)/whose eta (10) is two or more things differ on a concept.

By the time the value of eta (0.1)/eta (10) of the Plastic solid acquired from the above-mentioned fluorine-containing polymer acquires the above-mentioned Plastic solid from the above-mentioned fluorine-containing polymer, when not performing macromolecule quantification of bridge formation etc., it is substantially [as the value of eta (0.1)/eta (10) of the above-mentioned fluorine-containing polymer] the same.

[0045]

Although thermoplastics comes to flow above that melting point and the viscosity of a proper is shown, this viscosity changes with the stress at the time of measurement, and its relaxation times. Change of the above-mentioned viscosity can be measured using a melting viscoelasticity measuring device, and it is shown that the above-mentioned viscosity is dependent on a frequency. The frequency to which viscosity needs long time amount for stress relaxation in addition to regularity or viscosity becoming high in thermoplastics with higher molecular weight although it becomes almost fixed, namely, the above-mentioned viscosity generally becomes fixed [the above-mentioned viscosity] from a certain specific frequency which lowers the frequency becomes small. When some [at least] molecules of thermoplastics are ultrahigh-molecular-weight objects, even if it lowers a frequency, viscosity does not become fixed, but the phenomenon in which viscosity becomes still larger is seen as a frequency falls.

[0048]

Therefore, among the molecules of a fluorine-containing polymer, at least a part is an ultrahigh-molecular-weight object, and means that there are many these ultrahigh-molecular-weight objects, and, as for the value of Above eta (0.1)/eta (10) being large, that the value of Above eta (0.1)/eta (10) is small means that there are few ultrahigh-molecular-weight objects among the molecules of a fluorine-containing polymer.

When many ultrahigh-molecular-weight objects are included as a molecule of the above-mentioned fluorine-containing polymer, the Plastic solid which fabricates a fluorine-containing polymer and is acquired is strong to a mechanical strength, and the plastic deformation by being put to stress can be suppressed for a long period of time, and it excels in configuration stability. An above-mentioned fluorine-containing polymer is also one of this inventions.

[0047]

In order to make into above-mentioned within the limits eta (0.1)/eta (10) of the fluorine-

containing polymer used for the fluorine-containing Plastic solid manufacture approach (1) of this invention, it is desirable to manufacture a fluorine-containing polymer with wide width of face of molecular weight distribution and/or width of face of presentation distribution. The above "the width of face of presentation distribution is wide" means that the combination of the monomer which makes a fluorine-containing polymer is various between polymer chains, and/or that the rate of the monomer which makes a fluorine-containing polymer is various between polymer chains.

[0048]

As the preparation approach of preparing the above-mentioned fluorine-containing polymer,

(1) How to contact fluorine gas,

(2) How to change polymerization conditions in the middle of the polymerization of the above-mentioned compound (I),

(3) How to blend two or more sorts of fluorine-containing polymers from which the width of face of presentation distribution and/or the width of face of a molecular weight distribution differ, ** is mentioned.

[0049]

It is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer, for example as an approach of contacting the above-mentioned preparation approach (1) "fluorine gas", and the fluorine-containing polymer manufacture approach (henceforth "the fluorine-containing polymer manufacture approach (i)") of having the process at which fluorine gas is contacted etc. is mentioned.

[0050]

Although the process at which the above-mentioned fluorine gas is contacted can be performed like the fluoridization in the above-mentioned fluorine-containing Plastic solid manufacture approach (1), as for the fluoridization which performs to a fluorine polymer and is performed to the processing prefabrication object in the above-mentioned fluorine-containing Plastic solid manufacture approach (1), objects differ. Although it is not clear as a device in which the above-mentioned fluorine polymer changes with the fluoridization in the fluorine-containing polymer manufacture approach (i), the fluorine-containing polymer obtained Since the value of eta (0.1)/eta (10) is large compared with the above-mentioned fluorine polymer When the above-mentioned fluorine polymer contacts fluorine gas, a fluorine polymer molecule produces new association among other fluorine polymer molecules, or a fluorine polymer molecule produces new association in intramolecular, and it is thought that macromolecule quantification is carried out.

[0051]

that eta (0.1)/whose eta (10) is less than two as a fluorine polymer which performs the above-mentioned fluoridization, and the thing eta (0.1)/whose eta (10) is two or more — you may be any. Even if eta (0.1)/eta (10) is less than two fluorine polymer, eta (0.1)/eta (10) can obtain two or more fluorine-containing polymers by performing the above-mentioned fluoridization.

Like the fluoridization in the above-mentioned fluorine-containing Plastic solid manufacture approach (1), the above-mentioned fluoridization can remove the impurity which a fluorine polymer has, or can stabilize an unstable end group while it carries out macromolecule quantification of the fluorine polymer.

[0052]

the above-mentioned preparation approach (2) — "— the polymerization of the above-mentioned compound (I) — on the way — it is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer as approach" to which it appears and polymerization conditions are changed, for example, and the whole quantity of the above-mentioned compound (I) teaches, and the fluorine-containing polymer manufacture approach (henceforth "the fluorine-containing polymer manufacture approach (ii)") of having the process which makes a polymerization reaction starting etc. is mentioned.

[0053]

As for the above-mentioned compound (I), it is desirable to carry out copolymerization to an

ethylene nature monomer as mentioned above. As for the above-mentioned ethylene nature monomer, it is desirable to teach the part of the whole addition, before making optimum dose and a polymerization reaction start, and to add the remaining addition suitably during a polymerization reaction. Furthermore, when carrying out copolymerization to other copolymerizable monomers, it is also the same as that of the approach of adding the above-mentioned ethylene nature monomer.

[0054]

The ratio of the monomer in the system of reaction can be changed in the middle of a polymerization by making whole-quantity preparation and a polymerization reaction start the above-mentioned compound (I), and adding the above-mentioned ethylene nature monomer suitably during a polymerization reaction. Thus, by increasing a monomer in the middle of a polymerization, or reducing a monomer, polymerization conditions can be made to be able to change in the middle of a polymerization, width of face of the molecular weight distribution of the fluorine-containing polymer obtained and/or width of face of presentation distribution can be made large, and eta (0.1)/eta (10) of a fluorine-containing polymer can be made or more into two.

[0055]

the above-mentioned preparation approach (2) — "— the polymerization of the above-mentioned compound (I) — on the way — as approach" to which it appears and polymerization conditions are changed — except for the above-mentioned fluorine-containing polymer manufacture approach (ii) — a polymerization — on the way — the approach of coming out and changing polymerization temperature, and a polymerization — on the way — the approach of coming out and adding a polymerization initiator in large quantities, and a polymerization — on the way — the method of coming out and adding a chain transfer agent in large quantities etc. is mentioned.

[0056]

It is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer, for example as an approach of blending two or more sorts of fluorine-containing polymers from which the width of face of the above-mentioned preparation approach (3) "presentation distribution and/or the width of face of a molecular weight distribution differ", and the fluorine-containing polymer manufacture approach (henceforth "the fluorine-containing polymer manufacture approach (iii)") of having the process which blends a fluorine polymer (P) and a fluorine polymer (Q) etc. is mentioned.

[0057]

the above — a fluorine polymer — (— P —) — and — the above — a fluorine polymer — (— Q —) — the above — a fluorine polymer — (— P —) — it can set — the above — a compound — (— I —) — a unit — a mol — conversion — content — [— p — % —] — the above — a fluorine polymer — (— Q —) — it can set — the above — a compound — (— I —) — a unit — a mol — conversion — content — [— q — % —] — a ratio — [(p-q) — /— q —] (however, it is p>q.) — 0.5 — more than — it is — thing — it is — .

[0058]

In this specification, the above "a compound (I) unit" is a part of molecular structure of a fluorine polymer (P), is a part originating in a compound (I), and a part of molecular structure of a fluorine polymer (Q), and means the part originating in a compound (I). a book — a specification — setting — the above — "— a fluorine polymer — (— P —) — it can set — the above — a compound — (— I —) — a unit — a mol — conversion — content — [— p — % —] — " — a fluorine-containing copolymer — (— P —) — a molecule — it can set — all — a monomeric unit — originating — a monomer — a mol — the mol of the above-mentioned compound (I) with which the above-mentioned compound (I) unit occupied to a number [N] originates — a number [N] — comparatively — coming out — it is — the following type

pN(%) =(N1/N)x100

It comes out and the average of the content [pN (%)] expressed is meant.

[0059]

In this specification, the view about the mol conversion content of an above-mentioned

compound (I) unit and a compound (I) unit is similarly applied about a below-mentioned fluorine polymer (PT) and a below-mentioned fluorine polymer (QT).

the mol of the above-mentioned compound (I) unit — conversion content [%] — infrared absorption — they are a spectrum [IR] or the value acquired using the melting NMR in 300 degrees C.

[0060]

Although the rate which blends the above-mentioned fluorine polymer (P) and the above-mentioned fluorine polymer (Q) is based on the mol conversion content of the above-mentioned compound (I) unit in the mol conversion content and the above-mentioned fluorine polymer (Q) of the above-mentioned compound (I) unit in the above-mentioned fluorine polymer (P) if eta (0.1)/eta (10) of the fluorine-containing polymer obtained becomes two or more — fluorine polymer (P): — it is desirable that fluorine polymers (Q) are 1:9-9:1 in a solid content weight ratio.

[0061]

That the mol conversion rates of the above-mentioned compound (I) in a fluorine polymer (P) and a fluorine polymer (Q) differ means that the class of monomer which makes a fluorine polymer (P) differs from the class of monomer which makes a fluorine polymer (Q), and/or that the rate of the monomer which makes a fluorine polymer (P) differs from the rate of the monomer which makes a fluorine polymer (Q). By blending the fluorine polymer (P) and fluorine polymer (Q) whose ratio of mol conversion content of the above-mentioned compound (I) is 0.5 or more, eta (0.1)/eta (10) of the fluorine-containing polymer obtained can be made or more into two.

Although the thing eta (0.1)/whose eta (10) is less than two, respectively before the process which blends the above-mentioned fluorine polymer (P) and the above-mentioned fluorine polymer (Q), or eta (0.1)/eta (10) is two or more, it may be any.

[0062]

In the fluorine-containing polymer manufacture approach (iii), the process which blends the above-mentioned fluorine polymer (P) and the above-mentioned fluorine polymer (Q) may consist of blending further at least one sort of the fluorine polymer of others which are obtained by carrying out the polymerization of the above-mentioned compound (I). As for the mol conversion content of the above-mentioned compound (I) unit in the above and other fluorine polymers, it is desirable that it is a thing exceeding less than p % or q % in order to make large width of face of presentation distribution of a fluorine-containing polymer.

[0063]

As an approach of blending two or more sorts of fluorine-containing polymers from which the width of face of the above-mentioned preparation approach (3) "presentation distribution and/or the width of face of a molecular weight distribution differ" For example, it is the fluorine-containing polymer manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer in addition to the above-mentioned fluorine-containing polymer manufacture approach (iii). The fluorine-containing polymer manufacture approach of having the process which blends a fluorine polymer (R) and a fluorine polymer (S) (it is hereafter called "the fluorine-containing polymer manufacture approach (iv)".) It can use.

[0064]

The ratio [r/s] (however, it is r>s.) of the melt flow rate [r (g / 10 minutes)] of the above-mentioned fluorine polymer (R) and the melt flow rate [s (g / 10 minutes)] of the above-mentioned fluorine polymer (S) of the above-mentioned fluorine polymer (R) and the above-mentioned fluorine polymer (S) is ten or more.

[0065]

although the rate which blends the above-mentioned fluorine polymer (R) and the above-mentioned fluorine polymer (S) is based on the ratio of the melt flow rate of the above-mentioned fluorine polymer (R), and the melt flow rate of the above-mentioned fluorine polymer (S), if eta (0.1)/eta (10) of the fluorine-containing polymer obtained becomes two or more — fluorine polymer (R): — it is desirable that fluorine polymers (S) are 1:9-9:1 in a solid content weight ratio.

[0066]

That the ratio of the melt flow rate of a fluorine polymer (R) and a fluorine polymer (S) is ten or more means that the molecular weight of a fluorine polymer (R) differs from the molecular weight of a fluorine polymer (S) greatly. eta (0.1)/eta (10) can be made or more into two by blending the fluorine polymer (R) and fluorine polymer (S) whose ratio of a melt flow rate is ten or more. Although that eta (0.1)/whose eta (10) is less than two, respectively before the process which blends the above-mentioned fluorine polymer (R) and the above-mentioned fluorine polymer (S), and eta (0.1)/eta (10) are two or more, they may be any.

[0067]

In the fluorine-containing polymer manufacture approach (iv), the process which blends a fluorine polymer (R) and a fluorine polymer (S) may consist of blending further at least one sort of the fluorine polymer of others which are obtained by carrying out the polymerization of the above-mentioned compound (I). As for the melt flow rate of the above and other fluorine polymers, it is desirable that it is a thing exceeding under s (g / 10 minutes) or r (g / 10 minutes) in order to make large width of face of the molecular weight distribution of a fluorine-containing polymer.

[0068]

The above-mentioned fluorine-containing polymer manufacture approach as an approach of manufacturing a fluorine-containing polymer (i). Although eta (0.1)/eta (10) of a fluorine-containing polymer can be made or more into two even if it uses which approach among the fluorine-containing polymer manufacture approach (ii) fluorine-containing polymer manufacture approach (iii) and the fluorine-containing polymer manufacture approach (iv) It is desirable to use the fluorine-containing polymer manufacture approach (i) from the point which can stabilize the point and unstable end group which can make eta (0.1)/eta (10) two or more easily.

[0069]

The fluorine-containing polymer obtained by the fluorine-containing polymer obtained by the fluorine-containing polymer manufacture approach (i), the fluorine-containing polymer obtained by the fluorine-containing polymer manufacture approach (ii), the fluorine-containing polymer obtained by the fluorine-containing polymer manufacture approach (iii), and the fluorine-containing polymer manufacture approach (iv) is also one of this inventions.

[0070]

The above-mentioned fluorine-containing polymer used for the fluorine-containing Plastic solid manufacture approach (1) of this invention can also be used as a fluorine-containing polymer derivative by using the above-mentioned fluorine-containing polymer as a precursor. The fluorine-containing polymer which can be used as the above-mentioned precursor is a fluorine-containing polymer (T) obtained by carrying out the polymerization of the perfluoro vinyl ether derivative (T1) (henceforth "a compound (T1)") expressed with a general formula (II).

[0071]

Y1, Y2, n, and m in the above-mentioned general formula (II) of the above-mentioned compound (T1) are the same as that of the above-mentioned general formula (I). A2 in the above-mentioned general formula (II) expresses -SO 2X2 or -COZ2. X2 expresses a halogen atom or -NR one R2, and R1 and R2 are the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed.

[0072]

Although the same thing as the above Y1 and Y2 is mentioned as a halogen atom of the above X2, the halogen atom of the above X2, the halogen atom of Y1, and the halogen atom of Y2 may be the same, and may differ from each other. Preferably, it is a fluorine atom. The above R1 and R2 is the same as R1 and R2 in X1 of the above-mentioned general formula (I). As for the above X2, it is desirable that it is a halogen atom, and it is more desirable that it is a fluorine atom.

[0073]

The above Z2 expresses the alkoxyl group of -NR seven R8 or carbon numbers 1-4, the above R7 and R8 is the same — or it differs and a hydrogen atom, alkali metal, an alkyl group, or a sulfonyl content radical is expressed. The above R7 and R8 and an alkoxyl group are the same as R7, R8, and the alkoxyl group in Z1 of the above-mentioned general formula (I). As for the above Z2, it is desirable that it is the alkoxyl group of carbon numbers 1-4, and it is more desirable that

it is -OCH3.
[0074]
As the above-mentioned compound (T1), n in the above-mentioned general formula (II) is 0, and the thing whose m is 2, whose A2 is -SO 2X2 and whose X2 Y2 is a fluorine atom and is a fluorine atom is desirable.
[0075]
The above-mentioned fluorine-containing polymer derivative can be obtained by performing precursor processing by using the above-mentioned fluorine-containing polymer (T) as a precursor. The above-mentioned precursor processing is alkali hydrolysis or a thing which carries out acid treatment about the above-mentioned fluorine-containing polymer (T). It is not limited especially as alkali used for the above-mentioned alkali hydrolysis, for example, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium hydrogencarbonate, etc. are mentioned. By the above-mentioned alkali hydrolysis, the fluorine-containing polymer derivative whose end is the salt of a sulfonic group can be obtained, further, acid treatment may be performed and the salt of the sulfonic group of an end may be changed into a sulfonic group. It is not limited especially as an acid used for the above-mentioned acid treatment, for example, organic acids, such as inorganic-acid; formic acids, such as a hydrochloric acid, a sulfuric acid, and a phosphoric acid, an acetic acid, and a propionic acid, etc. are mentioned.
[0076]
As for the above-mentioned fluorine-containing polymer derivative, the above X2 or the above Z2 in the above-mentioned fluorine-containing polymer (T) is changed into -OM3 or -OM 41/2 by the above-mentioned precursor processing. Since the above-mentioned fluorine-containing polymer (T) carries out the polymerization of the above-mentioned compound (T1) and is obtained, the above X2 and the above Z2 in the above-mentioned fluorine-containing polymer (T) of it are the same as that of X2 in the above-mentioned general formula (II), and Z2 in the above-mentioned general formula (II). The above M3 expresses a hydrogen atom or alkali metal. It is not limited especially as the above-mentioned alkali metal, for example, the same thing as M1 in a general formula (I) etc. is mentioned, and the alkali metal of the above M1 and the alkali metal of M3 may be the same, and may differ from each other. The above M4 expresses alkaline earth metal. It is not limited especially as the above-mentioned alkaline earth metal, for example, the same thing as M2 in a general formula (I) etc. is mentioned, and the above M2 and M4 may be the same, and may differ. the alkali metal in the above M3, and the alkaline earth metal in the above M4 — the above-mentioned precursor processing — originating in the alkali used for the alkali hydrolysis to kick, the hydrogen atom in the above M3 originates in the acid used for the acid treatment in the above-mentioned precursor processing.
The above-mentioned fluorine-containing polymer derivative is also one of this inventions.
[0077]
The above-mentioned fluorine-containing polymer derivative can be obtained by adding "the process which carries out precursor processing" which performs the above-mentioned precursor processing to the approach of manufacturing an above-mentioned fluorine-containing polymer, respectively, although obtained by performing above-mentioned precursor processing to the above-mentioned fluorine-containing polymer (T).
[0078]
The fluorine-containing polymer derivative manufacture approach (A) is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative, and has the process at which fluorine gas is contacted, and the process which carries out precursor processing.
[0079]
The process at which the above-mentioned fluorine gas is contacted is the same as that of the fluoridization in the above-mentioned fluorine-containing polymer manufacture approach (i).
In the fluorine-containing polymer derivative manufacture approach (A), the process which carries out precursor processing may be performed before the process at which fluorine gas is contacted, and may be performed after the process at which fluorine gas is contacted.
[0080]

The fluorine-containing polymer derivative manufacture approach (B) is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative, teaches the whole quantity of the above-mentioned compound (T1), and has the process which makes a polymerization reaction start, and the process which carries out precursor processing.
[0081]
The above "the process which the whole quantity of a compound (T1) is taught [process] and makes a polymerization reaction start" can be performed like the above-mentioned fluorine-containing polymer manufacture approach (ii).
In the fluorine-containing polymer derivative manufacture approach (B), the process which carries out precursor processing is performed after the above "the process which the whole quantity of a compound (T1) is taught [process] and makes a polymerization reaction start."
[0082]
The fluorine-containing polymer derivative manufacture approach (C) is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative, and has the process which blends a fluorine polymer (PT) and a fluorine polymer (QT), and the process which carries out precursor processing.
[0083]
the above — a fluorine polymer — (— PT —) — and — the above — a fluorine polymer — (— QT —) — the above — a fluorine polymer — (— PT —) — it can set — the above — a compound (T1) — a unit — a mol — conversion — content — [— pt — % —] — the above — a fluorine polymer — (— QT —) — it can set — the above — a compound (T1) — a unit — a mol — conversion — content — [— qt — % —] — a ratio — [(pt-qt) — % —] (however, it is pt>qt.) — 0.5 — more than — it is — a thing — it is — .
[0084]
The process which blends the above-mentioned fluorine polymer (PT) and a fluorine polymer (QT) can be performed like the process which blends the above-mentioned above-mentioned fluorine polymer (P) and the above-mentioned above-mentioned fluorine polymer (Q) in the fluorine-containing polymer manufacture approach (iii).
Although it carries out after the process which may perform the process which carries out precursor processing in the fluorine-containing polymer derivative manufacture approach (C) before the process which blends a fluorine polymer (PT) and a fluorine polymer (QT), and blends a fluorine polymer (PT) and a fluorine polymer (QT), since the activity is efficient, it is desirable to carry out after the process which blends a fluorine polymer (PT) and a fluorine polymer (QT).
[0085]
The fluorine-containing polymer derivative manufacture approach (D) is the fluorine-containing polymer derivative manufacture approach which consists of manufacturing the above-mentioned fluorine-containing polymer derivative, and has the process which blends a fluorine polymer (RT) and a fluorine polymer (ST), and the process which carries out precursor processing.
[0086]
The ratio [rt/st] (however, it is rt>st.) of the melt flow rate [rt (g / 10 minutes)] of the above-mentioned fluorine polymer (RT) and the melt flow rate [st (g / 10 minutes)] of the above-mentioned fluorine polymer (ST) of the above-mentioned fluorine polymer (RT) and the above-mentioned fluorine polymer (ST) is ten or more.
[0087]
The process which blends the above-mentioned fluorine polymer (RT) and a fluorine polymer (ST) can be performed like the process which blends the above-mentioned above-mentioned fluorine polymer (R) and the above-mentioned above-mentioned fluorine polymer (S) in the fluorine-containing polymer manufacture approach (iv). Although it carries out after the process which may perform the process which carries out precursor processing in the fluorine-containing polymer derivative manufacture approach (D) before the process which blends a fluorine polymer (RT) and a fluorine polymer (ST), and blends a fluorine polymer (RT) and a fluorine polymer (ST), since the activity is efficient, it is desirable to carry out after the process which blends a fluorine polymer (RT) and a fluorine polymer (ST).

[0088]
The fluorine-containing polymer derivative obtained by the fluorine-containing polymer derivative obtained by the fluorine-containing polymer derivative manufacture approach (A), the fluorine-containing polymer derivative obtained by the fluorine-containing polymer derivative manufacture approach (B), the fluorine-containing polymer derivative obtained by the fluorine-containing polymer derivative manufacture approach (C), and the fluorine-containing polymer derivative manufacture approach (D) is also one of this inventions.
[0089]
In the fluorine-containing Plastic solid manufacture approach (1) of this invention, after using the above-mentioned fluorine-containing polymer as a molding material for mixing with the above-mentioned fluorine-containing polymer derivative, and fabricating a processing prefabrication object and fabricating it, it can contact fluorine gas and can acquire a fluorine-containing Plastic solid. The above-mentioned fluorine-containing Plastic solid can also use for, fabricate and obtain a fluorine-containing polymer derivative instead of the above-mentioned fluorine-containing polymer.
The fluorine-containing Plastic solid manufacture approach (2) which consists of fabricating using a fluorine-containing polymer derivative and acquiring a fluorine-containing Plastic solid is one of this inventions.
[0090]
The fluorine-containing Plastic solid manufactured by the fluorine-containing Plastic solid manufacture approach (1) of this invention and the fluorine-containing Plastic solid manufactured by the fluorine-containing Plastic solid manufacture approach (2) of this invention are also one of this inventions. The above-mentioned fluorine-containing Plastic solid manufacture approach (1) acquires a fluorine-containing Plastic solid using a fluorine-containing polymer, and the above-mentioned fluorine-containing Plastic solid manufacture approach (2) acquires a fluorine-containing Plastic solid using a fluorine-containing polymer derivative.
[0091]
The fluorine-containing Plastic solid of this invention follows, and is fabricated using the thing fabricated using the above-mentioned fluorine-containing polymer, and/or the above-mentioned fluorine-containing polymer derivative. A fluorine-containing polymer may be used independently and the above-mentioned fluorine-containing Plastic solid may fabricate it, a fluorine-containing polymer derivative may be used independently, and it may fabricate it, and may mix, use for and fabricate a fluorine-containing polymer and a fluorine-containing polymer derivative.
[0092]
Although it is not limited especially as a configuration of the fluorine-containing Plastic solid acquired by the fluorine-containing Plastic solid manufacture approach (1) of this invention, and the fluorine-containing Plastic solid acquired by the fluorine-containing Plastic solid manufacture approach (2) of this invention, for example, the shape of the shape of a globular shape, cylindrical, cylindrical, and hexahedron and film etc. is mentioned, when using a fluorine-containing Plastic solid as an electrolyte membrane or ion exchange membrane, it is usually the film-like.
[0093]
It is not limited especially as an approach of fabricating the above-mentioned fluorine-containing Plastic solid, for example, the melting fabricating method, the cast method, the sinking-in method, etc. are mentioned. The above-mentioned melting fabricating method is the approach of heating a fluorine-containing polymer to the temperature more than the melting point, and carrying out fabrication with means, such as a press and extrusion. The describing [above] cast method is the approach of exfoliating from a substrate the coat which substrates, such as glass, are made to usually apply and dry the solution made to come to dissolve a fluorine-containing polymer in solvents, such as a mixed solvent of alcohol and water, and is obtained. The above-mentioned sinking-in method is an approach of sinking into the solution which comes to dissolve a fluorine-containing polymer in solvents, such as a mixed solvent of alcohol and water, and making it drying base materials, such as fibrous material, such as a glass fiber and a carbon fiber, or textile fabrics of those, and porous matter. When manufacturing the film as the above-

mentioned fluorine-containing Plastic solid, it is desirable to use the above-mentioned sinking-in method.
[0094]
It fabricates using the above-mentioned fluorine-containing polymer and/or the above-mentioned fluorine-containing polymer derivative, and the fluorine-containing Plastic solid which is that whose thickness is 10-200 micrometers is also one of this inventions. The fluorine-containing Plastic solid which has the above-mentioned thickness is usually called the film, and since stress concentrates on a part with thin thickness and the above-mentioned film becomes easy to be torn, it is desirable to have smooth nature.
[0095]
Although not limited especially as an application of the above-mentioned fluorine-containing Plastic solid, using as film is desirable and an electrolyte membrane, ion exchange membrane, etc. are mentioned as the above-mentioned film, for example. Since the fluorine-containing Plastic solid acquired by the fluorine-containing Plastic solid acquired by the fluorine-containing Plastic solid manufacture approach (1) of this invention and the fluorine-containing Plastic solid manufacture approach (2) of this invention has the sulfonic group which may form the halo sulfonyl group or the salt in an end, it has a property desirable as an electrolyte membrane or ion exchange membrane.
[0096]
As an electrolyte membrane or an ion exchange membrane, the above-mentioned fluorine-containing Plastic solid can be used for for example, the film for electrolytes, the film for lithium cells, the film for brine electrolysis, the film for water electrolysis, the film for halide acid electrolysis, the film for oxygen enrichers, the film for humidity sensors, the film for gas sensors, a demarcation membrane, etc., and a service condition can use it suitably also in a usually severe fuel cell for a long period of time.
[0097]
It can use for a long period of time, without being hard to swell, and being torn or deforming plastically by the structure of cross linkage which the fluorine-containing Plastic solid acquired by the fluorine-containing Plastic solid and the fluorine-containing Plastic solid manufacture approach (2) which were acquired by the fluorine-containing Plastic solid manufacture approach (1) of this invention has, even if it is the case where the above-mentioned fluorine-containing Plastic solid is used as the cation exchange membrane for alkali electrolysis, or a diaphragm for fuel cells.
[0098]
A measuring method is explained about various kinds of elements currently hereafter used since a fluorine-containing polymer is specified. The data in an example and the example of a comparison are obtained by the above-mentioned measuring method.
[0099]
(eta (0.1)/eta (10))
A fluorine-containing polymer is fabricated on a sheet with a thickness of 1.5mm, and frequency dispersion with a viscosity of 270 degrees C is measured using a parallel plate with a RDS-II mold viscoelasticity measuring device (a trade name, product made from Rheometrics).
[0100]
(Mol conversion content)
It measures by the 19 F-NMR method, and asks for the mol conversion content of the monomer which makes a fluorine-containing polymer.
[0101]
(Melt flow rate)
Based on ASTM D 3159, it measures by the temperature of 270 degrees C, and 2.16kg of loads.
[0102]
[Example]
Although an example is given to below and this invention is explained to it in more detail, this invention is not limited only to these examples.
Example 1

It introduced until it taught 1490g of reverse osmotic membrane water, C7F15COONH4 30g, Na2HPO4 6.25g, NaH2PO4 3.94g, and CF2=CFOCF2CF2SO2F 60g to the proof-pressure container made from SUS-316 of 3l. of content volume equipped with the stirring aerofoil and the jacket for temperature control, it considered as the vacuum after nitrogen permuted the inside of a system, and internal pressure was set to 0.2MPa(s) in tetrafluoroethylene [TFE] after that. Temperature control was performed so that an internal temperature might become 55 degrees C, and TFE was further introduced so that internal pressure might serve as 0.8MPa(s). (NH4) What dissolved 2S2O8 3g in 10g water was introduced in the system, and the polymerization was started. Then, it doubled with the amount of TFE which added and added TFE so that internal pressure might maintain 0.8MPa(s), and CF2=CFOCF2CF2SO2F were taught by the addition so that it might be set to CF2=CFOCF2CF2SO2 F:TFE=0.418:1 by the weight ratio.

[0103]

After [of polymerization initiation] 166 minutes, when 594g of TFE(s) was introduced by the addition, pressure was discharged into TFE, and the polymerization was suspended. 140g of water was added to 70g of obtained polymerization liquid, it heated at 50 degrees C, and 7g of concentrated hydrochloric acid was supplied. After filtering the coagulated polymer, re-distribution and filtration of water were repeated 3 times, and it dried with the air forced oven.

[0104]

the ratio of the reinforcement which belongs to the fluorine atom of the underline section of -OCF2CF2- near -80 ppm when 19 F-NMR is measured at 300 degrees C about the obtained polymer, and the reinforcement which belongs to the fluorine atom of the underline section of -CF2CF2- near -125 ppm to CF2=CFOCF2CF2SO2F — 13-mol% — it turned out that it was introduced.

[0105]

After it carried out the temperature up to 200 degrees C and fluorine:nitrogen contacted the gas of 20:80 by the volume ratio at 200 degrees C after that at a part for 0.6l./for 5 hours, putting obtained polymer 10g into the oven made from a Monel metal, and circulating nitrogen gas, it cooled to the room temperature, circulating nitrogen gas. When the obtained polymer was fabricated on the sheet with a thickness of 1.5mm and the frequency dispersion of viscosity was measured at 270 degrees C using the parallel plate with the RDS-II mold viscoelasticity measuring device (a trade name, product made from Rheometrics), it was eta(0.1)/eta(10) =13.5.

[0106]

The example 1 of a comparison

When the polymer was fabricated on the sheet with a thickness of 1.5mm, without carrying out the fluoridization and the frequency dispersion of viscosity was measured like the example 1 about the polymer obtained in the example 1, it was eta(0.1)/eta(10) =1.7.

[0107]

In the example 1 of a comparison which did not perform the fluoridization to a polymer in the example 1 which performed the fluoridization to eta (0.1)/eta (10) having been a value higher than 2, it turned out that eta (0.1)/eta (10) was a value lower than 2.

[0108]

Example 2

It introduced until it taught 1490g of reverse osmotic membrane water, C7F15COONH4 30g, Na2HPO4 6.25g, NaH2PO4 3.94g, and CF2=CFOCF2CF2SO2F 300g to the proof-pressure container made from SUS-316 of 3L of content volume equipped with the stirring aerofoil and the jacket for temperature control, it considered as the vacuum after nitrogen permuted the inside of a system, and internal pressure was set to 0.2MPa(s) in TFE after that. Temperature control was performed so that an internal temperature might become 50 degrees C, and TFE was further introduced so that internal pressure might serve as 0.8MPa(s). (NH4) What dissolved 2S2O8 3g in 10g water was introduced in the system, and the polymerization was started. Then, TFE was added so that internal pressure might maintain 0.8MPa(s).

[0109]

After [of polymerization initiation] 151 minutes, when 522g of TFE(s) was introduced by the addition, pressure was discharged into TFE, and the polymerization was suspended. 140g of

water was added to 70g of obtained polymerization liquid, it heated at 50 degrees C, and 7g of concentrated hydrochloric acid was supplied. After filtering the coagulated polymer, re-distribution and filtration of water were repeated 3 times, and it dried with the air forced oven.

[0110]

the ratio of the reinforcement which belongs to the fluorine atom of the underline section of -OCF2CF2- near -80 ppm when 19 F-NMR is measured at 300 degrees C about the obtained polymer, and the reinforcement which belongs to the fluorine atom of the underline section of -CF2CF2- near -125 ppm to CF2=CFOCF2CF2SO2F — 15.6-mol% — it turned out that it was introduced.

[0111]

When the obtained polymer was fabricated on the sheet with a thickness of 1.5mm and the frequency dispersion of viscosity was measured like the example 1, it was eta(0.1)/eta(10) =5.1.

[0112]

In the example 2 which changed polymerization conditions to the polymer in the middle of the polymerization to eta (0.1)/eta (10) having been 13.5 in the example 1 which performed the fluoridization, it turned out that eta (0.1)/eta (10) was 5.1 and a value lower than an example 1.

[0113]

[Effect of the Invention]

Since a fluorine-containing polymer and its manufacture approach have an above-mentioned configuration in the fluorine-containing Plastic solid of this invention and its manufacture approach, and a list, they can acquire the fluorine-containing Plastic solid excellent in the configuration stability over plastic deformation etc. in them.

[Translation done.]